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19 ABSTRACT (Continue on reverse if necessary and identify by block number)

Metal complexes and solids were synthesized and subjected to photoexcitation measurements under the influence of externally applied magnetic fields. The photoluminescence of complexes of rhodium(I) and iridium(I) displayed both field-induced emission bands and a many-fold shortening of the excited state lifetime. Both the decay rates and the induced emission band intensities showed a quadratic dependence on the applied field. A several-fold shortening of the phosphorescence from the octaphosphitoplatinum(II) anion under an applied field (50 T) was also observed. Spectroscopic studies of several bis(N-heterocyclic) complexes of copper(I) were also concluded and complete group-theoretic assignments of the charge-transfer excited states were made. The technique of Thermal Modulation was perfected and applied to the study of the excited states of transition-metal complexes with near-degenerate emitting states. (KW)

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OFFICE OF NAVAL RESEARCH

FINAL REPORT

for

Contract N00014-87-K-0444

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Luminescence in Applied Magnetic Fields

TECHNICAL REPORT NO. 9

G. A. Crosby

Washington State University
Department of Chemistry
Pullman, WA 99164-4620

August 15, 1989

FINAL REPORT FOR THE PERIOD: 16 May 1987 - 15 May 1989

For Contract N00014-87-K-0444, R & T Code 4131031-3

Summary of Research Accomplishments

The goal of the research was to synthesize molecules and solids that display macroscopic changes of their optical properties as a function of externally applied magnetic fields. During the tenure of the grant we have made considerable progress toward this goal.

The technique of Thermal Modulation Emission Spectroscopy was developed and refined and the utility of this technique for the study of near-degenerate states in luminescent metal complexes was demonstrated. Particularly significant were the findings that the TME method could incorporate either a resistance heater or an IR laser for the thermal pulses. These results, including a mathmatical treatment of the origin of the TME signal, are reported fully in Technical Report #5.

In Technical Report #6 we described a study of four complexes of iridium(I) and rhodium(I) that manifest induced emission bands and shortening of the luminescence lifteimes as a function of an externally applied magnetic field. The induced spectra were shown to be proportional to B^2 while the decay times were observed to be inversely proportional to this quantity. A model based on available metal d- and p-orbitals and low-lying empty π-orbitals was adequate to rationalize the results.

A thorough study of the optical properties of a series of bis(N-heterocyclic) complexes of copper(I) was completed. Assignments were made of the states responsible for the visible absorption spectrum and also for the luminescence. The strong temperature dependence of the latter was rationalized in terms of a ^3E state arising from a ligand-to-metal charge transfer configuration that is split in first order by spin-orbit coupling. Reduction of the symmetries of the species from D_{2h} to D_2 was invoked to explain the finer details of both the emission and absorption spectra. A complete account of this study is contained in Technical Report #7.

Several zinc complexes were also evaluated as possible candidates for magnetic field studies. Particularly important was to find likely candidates for modifying radiationless rates by externally applied fields. No good candidates were found; but, during the course of the investigations we discovered that many of the solids underwent phase transitions. Although subtle, these phase changes drastically affected the emissive properties of the molecules. A thorough investigation of the phenomenon is reported in Technical Report #8 (which has recently been submitted for publication).

The most recent results of the research involve the measurement of the decrease in decay time of the phosphorescence of the octaphosphitodiplatnimum(II) anion as a function of the strength of an externally applied magnetic field. Moreover, the dramatic decrease was accounted for quantitatively by invoking spin-orbit coupling within the context of the previously published orbital scheme for the complex ion. These results are being readied for publication and will be submitted as Technical Report #10.

Technical Papers Published

TR-#5: G. A. Crosby and K. J. Jordan, "Applications of Thermal Modulation in Luminescence Spectroscopy", Proceedings of SPIE 743, 25-28 (1987).

TR-#6: C. A. Helms, T. A. Reynolds, G. A. Crosby, "External Magnetic Field Effects on the Excited States of Iridium(I) and Rhodium(I) Complexes", Chemical Physics Letters, 142, 99-102 (1987).

TR-#7: W. L. Parker and G. A. Crosby, "Assignment of the Charge-Transfer Excited States of Bis(N-Heterocyclic) Complexes of Copper(I)", Journal of Physical Chemistry, 93, 5692-5696 (1989).

Other Technical Reports

TR-#8: K. J. Jordan, W. F. Wacholtz, G. A. Crosby, "Structural Dependence of the Luminescence from Bis(substituted-benzenethiol)(2,9-dimethyl-1,10-phenanthroline)zinc(II) Complexes", submitted for publication.

End-of-the-Year Report: For the period 5/16/87 - 7/31/87
End-of-the-Year Report: For the period 8/1/87-7/15/88

Theses and Dissertations

C. A. Helms, "Effects of External Magnetic Fields on the Excited States of $(nd)^8$ Metal Complexes, Ph.D. Dissertation, 1988.

T. R. Reynolds, "Synthesis and Spectroscopic Investigations of Bis(chelated) Complexes of Platinum(II)", M.S. Thesis, Washington State University, (Sep 1989).

K. J. Jordan, "Part A: Structural Perturbations of the Electronic Excited States of Zinc Complexes. Part B: Construction of a Thermal Modulation Emission Apparatus", Ph.D. Dissertation, Washington State University, (Sep 1989).

G. R. Gamble, "Spectroscopic Investigations of Closed-Shell Transition-Metal Complexes", Ph.D. Dissertation, Washington State University, (Sep 1989).

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